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(54) CATALYST FOR ADDITION REACTION OF ALKYLENE OXIDE

(57) Abstract:

PROBLEM TO BE SOLVED: To provide a catalyst for addition reaction of alkylene oxide by which an alkylene oxide addition product with specific carbonyl value(COV) is obtained and of which catalyst activity is excellent, a method to produce the catalyst and a method to produce the alkylene oxide addition product by using the catalyst.

SOLUTION: A catalyst is expressed by a general formula (I), wherein M is at least one bivalent metal of Mg, Zn, Ca, Ba, Fe, Co, Mn, Ni, Sr, Pd, Cd, Sn, Pt, Pb and Be; Q is at least one trivalent metal of Al, Sb, Fe, Co, and Cr; m is zero or more; 0<y<1, and is prepared in such a way that a catalyst precursor is baked which as been obtained by mixing a solution containing an ion expressed by M2+ and an ion expressed by Q3+ with alkali agent in 45°C or lower. The carbonyl value(COV) of an alkylene oxide addition product is 5 μ m mol/g or less.

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CLAIMS

[Claim(s)]

[Claim 1] General formula which comes to calcinate the catalyst precursor which mixes the solution and alkali chemicals containing the ion expressed with M2+, and the ion expressed with Q3+ below 45 degrees C, and is obtained (I): M1-y, Qy, and Oy+2/2 and mH2 O (I)

(M shows among a formula at least one kind of divalent metal chosen from Mg, Zn, calcium, Ba, Fe, Co, Mn, nickel, Sr, Pd, Cd, Sn, Pt, Pb, and Be, and Q shows at least one kind of trivalent metal chosen from aluminum, Sb, Fe, Co, and Cr.) m shows zero or more numbers. y shows the number of 0 < y < 1. Catalyst for alkylene oxide addition reactions expressed.

[Claim 2] A catalyst precursor is general formula (II):[M2+1-x Q3+x (OH)2]x+(An-) x/n and pH2 O. (II)

(M and Q are the same as that of the above among a formula, and An-shows the anion radical of n ** of the alkali-chemicals origin.) When A is plurality, n shows the total value of the valence of A. Moreover, n shows the integer of 1-3. p shows zero or more numbers and x shows the number of 0.1 <= x <= 0.5. Catalyst according to claim 1 expressed.

[Claim 3] The manufacture approach of the catalyst for alkylene oxide addition reactions of obtaining the catalyst precursor expressed with the general formula (II) specified in claim 2 which mixes the solution and alkali chemicals containing the ion expressed with M2+, and the ion expressed with Q3+ below 45 degrees C, and is obtained, and subsequently calcinating it.

[Claim 4] The manufacture approach of the alkylene oxide adduct which makes alkylene oxide add to the organic compound which has active hydrogen under existence of a catalyst according to claim 1 or 2.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the catalyst for alkylene oxide addition reactions and its manufacture approach, and the manufacture approach of the alkylene oxide adduct which uses the catalyst concerning a list.

[0002]

[Description of the Prior Art] As an example of the compound metal catalyst used for the reaction for which alkylene oxide is made to add to the organic compound which has active hydrogen, such as alcohol and a phenol, the catalyst which consists of a hydrotalcite compound containing Mg and aluminum is known (Patent Publication Heisei No. 503946 [five to] official report). Here, from a viewpoint of raising the crystallinity of a compound to the list which speeds up the synthesis rate of a compound, it is made to react above 50 degrees C, and the catalyst is prepared.

[0003] However, this catalyst was not what should be satisfied in respect of generation of the point of catalytic activity, and a by-product.

[0004]

[Problem(s) to be Solved by the Invention] The technical problem of this invention is offering the catalyst for alkylene oxide addition reactions with good catalytic activity which can obtain the alkylene oxide adduct whose carbonyl value's (COV's) is below 5micromol/g and its manufacture approach, and the manufacture approach of the alkylene oxide adduct which uses the catalyst concerning a list.

[0005]

[Means for Solving the Problem] This invention is a general formula (I) which comes to calcinate the catalyst precursor which mixes the solution and alkali chemicals containing the ion expressed with M2+, and the ion expressed with Q3+ below 45 degrees C, and is obtained. : M1-y, Qy, and Oy+2/2 and mH2 O (I)

(M shows among a formula at least one kind of divalent metal chosen from Mg, Zn, calcium, Ba, Fe, Co, Mn, nickel, Sr, Pd, Cd, Sn, Pt, Pb, and Be, and Q shows at least one kind of trivalent metal chosen from aluminum, Sb, Fe, Co, and Cr.) m shows zero or more numbers. y shows the number of 0< y<1. It is related with the catalyst for alkylene oxide addition reactions expressed and its manufacture approach, and the manufacture approach of the alkylene oxide (henceforth AO) adduct which used this for the list.

[0006]

[Embodiment of the Invention] The catalyst precursor concerning the catalyst (henceforth a catalyst (I)) expressed with the general formula (I) of preparation of catalyst> this invention It is obtained as precipitate (compound hydroxide) by mixing the solution (henceforth metal ion content liquid) and alkali chemicals containing the ion expressed with M2+, and the ion (M and Q expressing said same semantics) expressed with Q3+ below 45 degrees C. This catalyst precursor is general formula (II):[M2+1-x Q3+x (OH)2]x+(An-) x/n and pH2 O preferably. (II)

(M and Q are the same as that of the above among a formula, and An-shows the anion radical of n ** of the alkali-chemicals origin.) When A is plurality, n shows the total value of the valence of A. Moreover, n shows the integer of 1-3. p shows zero or more numbers and x shows the number of 0.1 <= x <= 0.5. It is expressed.

[0007] As ion expressed with M2+ here, Mg2+ and/or Zn2+ are desirable, and aluminum3+ is desirable as ion expressed with Q3+. That is, as for a catalyst precursor, it is desirable that it is the compound hydroxide which consists of Mg/aluminum, Zn/aluminum, or Mg/Zn/aluminum. In addition, the structure of (I) and (II) is searched for by the X-ray powder diffractometry.

[0008] Although the nitrate of each of said metal, acetate, a sulfate, a chloride salt, etc. may use any for preparation of metal ion content liquid, the viewpoint of catalytic activity to a nitrate is desirable. As a solvent which dissolves a metal salt, organic solvents, such as a methanol besides water, such as ion exchange water usually used, ethanol, and ethylene glycol, may be used, and you may be such mixture. The anything which produces precipitate by mixing with metal ion content liquid, alkali chemicals are OH, for example, although it is good. - The compound which has ion, or the mixture or either which has An-ion is mentioned. When using as mixture, coincidence supply is respectively carried out as mixture of both compounds, and it is used for preparation of a catalyst precursor. As An-ion, the anion of at least one sort of oxygen acid chosen from S, Se, Te, P, Si, germanium, Sn, B, V, Cr, Mo, W, Mn, Ru, Rh, Os, and U or metal halogen acid, S2-, CO3 2-, or Cs3 2- is illustrated. From a viewpoint of catalytic activity, the mixture of a sodium hydroxide, and a sodium carbonate or a sodium sulfate especially a sodium

carbonate is mentioned as desirable alkali chemicals. Although which gestalt of a solid or a water solution is sufficient as the supply gestalt of alkali chemicals, the homogeneous viewpoint of a reaction to its water solution is desirable. In addition, the catalytic activity said to this invention means the operation ability to the labile and selectivity of AO addition reaction.

[0009] The quantitative ratio of the ion expressed with M2+ in metal ion content liquid and the ion expressed with Q3+ is a mole ratio, are 1:1-9:1 preferably, and are 1:1-5:1 more preferably. OH in alkali chemicals - The quantitative ratio of the compound which has ion, and the compound which has An-ion will not be especially limited, if a desired catalyst precursor, as a result a desired catalyst are acquired. Moreover, especially similarly it is not limited about a ratio with the total quantity of the total quantity of the ion expressed with M2+ in the metal ion content liquid at the time of catalyst precursor preparation, and the ion expressed with Q3+, OH-ion contained in alkali chemicals, and An-ion.

[0010] Metal ion content liquid and alkali chemicals are supplied to a predetermined reaction vessel, stirring mixing is carried out, and both precipitation reaction performs preparation of a catalyst precursor. It is desirable to carry out from a viewpoint of catalytic activity, adding metal ion content liquid and alkali chemicals to coincidence, adjusting the addition rate of alkali chemicals, and keeping pH of mixed liquor constant. As for the pH value kept constant, it is desirable to change with metal components and to set up in pH=9-11 the case of Mg, and/or Zn and aluminum. From a viewpoint of catalytic activity, 45 degrees C or less, preferably, this precipitation reaction is -15-10 degrees C most preferably, and is performed -20-20 degrees C 30 degrees C or less for about 1 to 5 hours. Subsequently, supply of metal ion content liquid and alkali chemicals is suspended by request for about 1 to 20 hours, and it ripes on the same conditions as a precipitation reaction.

[0011] Although it was possible to have prepared a catalyst precursor below 45 degrees C conventionally, preparation of the catalyst precursor in this temperature region was not performed from a viewpoint of raising the crystallinity of a precursor to the list which brings the synthesis rate of a precursor forward. It became possible by on the other hand newly preparing a catalyst precursor in this invention based on a header and this knowledge by the reaction in the low temperature of 45 degrees C or less for saying [that the activity of a catalyst changes with preparation temperature remarkably] to prepare the catalyst which has the effectiveness of a request of this invention.

[0012] the catalyst precursor which separated from the solvent metal ion content liquid and the catalyst precursor obtained by mixing of alkali chemicals by approaches, such as filtration and centrifugal separation, and was obtained -- water -- it washes using ion exchange water preferably. The target catalyst is acquired by making it dry at 80-120 degrees C after washing, calcinating 400-1000 degrees C at 500-800 degrees C more preferably, and considering as an oxide preferably, in an inert gas air current and air or under a vacuum. It cools in inert gas or a vacuum, and, as for the catalyst after baking, it is desirable after cooling to be immersed in the organic compound (henceforth an active hydrogen compound) or AO adduct which has active hydrogen used for a reaction in order to prevent adsorption of water or a carbon dioxide.

[0013] It can also use by using a catalyst (I) as a Plastic solid again. Shaping receives a catalyst (I) or a catalyst precursor. As a binder for shaping Only water Or water, alumina sol, a silica sol, an antimony sol, a titanium sol, One or more sorts of the inorganic binders or ethanol chosen from the group of a zirconia sol, A water solution with organic binders, such as a methanol, ethylene glycol, a glycerol, and fatty alcohol It is preferably carried out especially 0.5 to 40% of the weight 50 or less % of the weight among the mixture of a catalyst (I) or a catalyst precursor, and the binder for shaping by adding 0.5- 30% of the weight preferably. Kneading with the binder for shaping can be performed, for example using a well-known kneader etc., and can perform shaping, for example with well-known extrusion molding, making tablet shaping, etc. It dries and calcinates on the above-mentioned conditions after shaping.

[0014] AO addition reaction said to <AO addition reaction> this invention means the reaction for which AO is made to add to an active hydrogen compound. The catalyst of this invention has high catalytic activity, and it may raise labile and selectivity in this AO addition reaction. Since labile can be maintained sufficiently highly, the amount of the catalyst used in reaction time can be lessened, and the load to a catalyst separation process can be reduced. Furthermore, since the selectivity of AO addition reaction is high, in case the COV value of AO adduct can be more preferably made below into 3.5micromol/g below 5micromol/g, AO adduct is used as a raw material and a derivative is manufactured, generating of the side reaction which is not desirable can be controlled. In addition, a COV value is measured by the approach of a publication in the below-mentioned example.

[0015] As an active hydrogen compound used for AO addition reaction, one or more sorts of alcohols, phenols, polyols, carboxylic acids, thiols, amines, and amides are mentioned. In these, alcohols are desirable, as these alcohols, the first class of the straight chain of carbon numbers 2-30 or branched chain or the second class alcohol is desirable, and the first-class alcohol of carbon numbers 6-24 is more desirable. Specifically, lauryl alcohol, myristyl alcohol, palmityl alcohol, stearyl alcohol, etc. can be mentioned.

[0016] Moreover, although what kind of thing is sufficient as it as long as AO reacts with an active hydrogen compound and can generate an adduct, that [its] to which epoxidation of the carbon with which carbon numbers 2-8 adjoin was carried out is desirable, and ethyleneoxide (henceforth EO), propylene oxide, or especially such mixture are desirable.

[0017] Although any formats, such as a stirred-tank-type batch process, a stirred-tank-type circulation type, and a fixed-bed circulation type, can be used for it, the reactor of AO addition reaction has a desirable fixed-bed circulation type, if the complicatedness of catalyst separation recovery etc. is taken into consideration.

[0018] In use with a batch process reactor, the amount of the catalyst used of this invention has desirable 0.05 - 20 weight section to the active hydrogen compound 100 weight section, and its 0.1 - 8 weight section is usually more desirable. Since a product will decompose if too high [when too low, a reaction rate is slow, and], 80-230 degrees C of 120-180 degrees C of reaction temperature are 120-160 degrees C especially preferably more preferably. Although reaction

pressure is based also on reaction temperature, it is 0.1 - 1MPa absolute pressure more preferably below 2MPa absolute pressure.

[0019] When it is powdered and uses a catalyst in AO addition reaction, an active hydrogen compound and a catalyst are taught by said ratio into a reactor, after introducing 0.1-100 mol of AO(s) and making them react preferably to one mol of active hydrogen compounds in nitrogengas-atmosphere mind under predetermined temperature and flow and pressure requirement, it can cool and AO adduct can be obtained by carrying out a catalyst a ** exception. moreover, when use a catalyst as a Plastic solid, a shaping catalyst be put into the stirring aerofoil which have the basket made with the wire made from stainless steel etc., and this and an active hydrogen compound be teach to a reactor, and after introduce AO and make it react in nitrogen gas atmosphere mind under predetermined temperature and flow and pressure requirement, it can carry out by extract only AO adduct cool and generated.

[0020] In manufacturing AO adduct by the fixed-bed circulation formula, the reactor of for example, a fixed-bed circulation type is filled up with a catalyst, and it dips AO for AO and an active hydrogen compound as a rate of 0.1-10 mols preferably to one mol of active hydrogen compounds. As for a dipping rate, 0.1-100h-1 is desirable at liquid space velocity, 0.2-70h-1 is more desirable, and especially 1-50h-1 is desirable. Especially a coil pressure is good at well-known extent which is not limited and is usually carried out. Below 3MPa absolute pressure is specifically desirable, 0.2 - 2MPa absolute pressure is more desirable, and especially 0.2 - 1MPa absolute pressure is desirable. 50-300 degrees C of reaction temperature are desirable, its 80-250 degrees C are more desirable, and especially its 100-230 degrees C are desirable. low-grade as AO -- AO, in using especially EO, in order to avoid the danger of the explosion, it is desirable to carry out to the bottom of nitrogen-gas-atmosphere mind.

[0021] When it carries out by this fixed-bed circulation formula, the component metal of a catalyst is not contained in AO adduct obtained, but the separation processing by filtration, centrifugal separation, etc. of AO adduct and a catalyst is unnecessary for it in it after a reaction.

[0022]

[Example] About the mixed solution which dissolved 0.5 mol/L and aluminum(NO3) 3 and 9H2 O for example 1 [catalyst preparation] Zn(NO3) 2 and 6H2 O in water at a rate of 0.2 mol/L, it is 0.24 mol/LNa2 CO3. A water solution and 4Ns With the NaOH water solution, coincidence supply was carried out at the reaction vessel of 10L volume by the volume of 25 mL/min, 18 mL/min, and 10 - 15 mL/min, respectively. Water 1L is beforehand put into the reaction vessel, and it stirred by 300rpm with the fixed-speed stirrer. A reaction vessel is cooled with a refrigerant from the exterior, and reaction mixture is kept at 5 degrees C, and it was made to ripe for 1 hour, suspending supply of each water solution and stirring suspension, after performing a precipitation reaction for 2 hours, where the addition of a NaOH water solution is adjusted so that it may be set to pH 9.7-10.3. Suspension was filtered after that and the obtained white solid-state was fully washed using ion exchange water. The catalyst precursor of the shape of a white solid-state which is dried in a 110-degree C warm air oven after washing for 12 hours, and is expressed with following type:[Zn5/7 aluminum2/7 (OH)2] (CO3) 1/7, and 2.7H2 O was

obtained. Subsequently, 550 degrees C of catalyst precursors after desiccation were calcinated in N2 air current for 2 hours, and the catalyst was acquired.

[0023] [Manufacture of AO adduct] After nitrogen permuted the inside of 4 weight sections preparation and a system to the 100 alcoholic weight sections, the temperature up of lauryl alcohol 500g and the above-mentioned catalyst was carried out to the 3.5L autoclave to 165 degrees C, carrying out low-speed stirring by 300rpm. It is EO at this temperature. It introduced maintaining 213g at pressure 0.36MPa, and reacted. Labile was 6.5 mol-EO/(mol-alcohol andh). It cooled at 110 degrees C and the catalyst was carried out the ** exception. Moreover, the COV value of AO adduct measured with the following measuring method was 2micromol/g.

[0024] The <COV measuring method> AO adduct was made to color by the 2, 4-dinitrophenylhydrazine, the absorbance was measured by 435nm, from the calibration curve, it asked for the number of mumol of the carbonyl compound in 1g of samples, and it was made into the COV value.

[0025] Except making temperature at the time of an example 2 - 4 catalyst-precursor preparation into 15 and 30 or 45 degrees C, the catalyst was prepared like the example 1 and AO adduct was obtained similarly. A result is shown in Table 1 and 2.

[0026] Example 5Mg(NO3) 2 and 6H2 O It is the mixed solution which dissolved 192.3g, and aluminum(NO3) 3 and 9H2 O120.8g in 1315g of ion exchange water 0.24 mol/L Na2 CO3 A water solution and 4Ns With the NaOH water solution, coincidence supply was carried out at the reaction vessel of 10L volume by the volume of 12.5 mL/min, 9 mL/min, and 5 - 7.5 mL/min, respectively. 500g of water is beforehand put into the reaction vessel, and it stirred by 250rpm with the fixed-speed stirrer. After it carries out temperature control of it so that whenever [solution temperature] may become 15 degrees C, it adjusted the addition of a NaOH water solution so that it may be further set to pH 9.7-10.3, and it performed a precipitation reaction for 2 hours, reaction mixture suspends supply of each water solution, and it was ripened for 1 hour, with suspension stirred. This suspension was filtered and the obtained white solid-state was fully washed using ion exchange water. It was made to dry in a 110-degree C warm air oven after washing for 12 hours, and the white solid-state-like catalyst precursor was obtained. Subsequently, it is a catalyst precursor after desiccation N2 In the air current, it calcinated for 2 hours and 550 degrees C of catalysts were acquired. Using the acquired catalyst, except making the amount of preparation catalysts into the 0.2 weight section, the same actuation as an example 1 was performed, and AO adduct was obtained. A result is shown in Table 1 and 2.

[0027] Example 6Zn(NO3) 2 and 6H2 O 55.8g, aluminum(NO3) 2 and 9H2 O Mg(NO3) 2 and [112.5g and] 6H2 O The mixed solution which dissolved 144.2g in 1299g of ion exchange water 0.24 mol/L Na2 CO3 A water solution and 4Ns With the NaOH water solution, the reaction vessel of 5L volume was supplied by the volume of 12.5 mL/min, 9 mL/min, and 5 - 7.5 mL/min, respectively. 500g of water is beforehand put into the reaction vessel, and it stirred by 250rpm with the fixed-speed stirrer. After it carries out temperature control of it so that whenever [solution temperature] may become 15**2 degrees C, it adjusted the addition of a NaOH water solution so that pH may be further set to 9.7-10.3, and it performed a precipitation

reaction for 2 hours, reaction mixture suspends supply of each water solution, and it was ripened for 1 hour, with suspension stirred. This suspension was filtered and the obtained white solid-state was fully washed using ion exchange water. It was made to dry in a 110-degree C warm air oven after washing for 12 hours, and the white solid-state-like catalyst precursor was obtained. Subsequently, it is a catalyst precursor after desiccation N2 In the air current, it calcinated for 2 hours and 550 degrees C of catalysts were acquired. Using the acquired catalyst, except making the amount of preparation catalysts into the 0.2 weight section, the same actuation as an example 1 was performed, and AO adduct was obtained. A result is shown in Table 1 and 2.

[0028] Except making the example 1 of a comparison, and temperature at the time of 2 catalyst-precursor preparation into 60 or 80 degrees C, the catalyst was prepared like the example 1 and AO adduct was obtained similarly. A result is shown in Table 1 and 2.

[0029] Except making temperature at the time of example of comparison 3 catalyst-precursor preparation into 60 degrees C, the catalyst was prepared like the example 5 and AO adduct was obtained similarly. A result is shown in Table 1 and 2.

[0030] Except making temperature at the time of example of comparison 4 catalyst-precursor preparation into 80 degrees C, the catalyst was prepared like the example 5 and AO adduct was obtained similarly. A result is shown in Table 1 and 2.

[0031]

[Table 1]

極媒組成式	2ns/1Al2/10s/1 · mH20	Zns/7Al2/70s/7 · pH20	Zns/1Al2/10s/1 • qH20	Zn6/7Al2/108/7 · rH20	Mgo. 7A10. 801. 15 · SHg0	0 Zn16/28Mg6/28Al6/2808/7 • tH20	Zns/1A12/108/1 • uH20	Zns/7Al2/70s/7 • vHs0	Mgo. 7Alo. 301. 15 • WH20	Mge. 7Ale. 801. 15 . ZH20
触媒前駆体組成式	[Zns/1A]2/1(0H)2](COs)1/1 · 2. 7H20	1	1	1	[Mgo. 1A] o. 3 (OH) 2] (CO3) o. 16 · aH20	[(Zno. 26Mgo. 75)6/Al2/7(OH)2](CO3)1/7 · CH2O	I		1	1
触媒前駆体 調製温度 (°C)	က	1 5	3.0	4.5	1.5	1.5	0 9	8 0	0 9	0 8
		27 El 25	က	4	ည	9	٠٠.	χ <u>ε</u>	က	4
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表中、触媒前駆体組成式、触媒組成式におけるHgOの係数はそれぞれ0より大きい数を示す。

[0032]

[Table 2]

		触媒前駆体 調製温度 (°C)	AO付加反応の反応活性 [mol-EO/(mol- アルコール・h)]	AO付加体の COV (μmol/g)
実	1	5	6. 5	2. 0
実施例	2	1 5	4. 5	3. 0
	3	3 0	3. 3	4. 3
	4	4 5	2. 3	4. 8
	5	1 5	2. 3	1. 3
	6	1 5	2. 2	1. 4
比較例	1	6 0	1. 1	9. 1
例	2	8 0	0. 3	1 2
	3	6 0	1. 0	4. 2
	4	8 0	0.82	4. 3

[0033] The catalyst which prepared and obtained the catalyst precursor below 45 degrees C has good catalytic activity, and according to this catalyst, a COV value can manufacture AO adduct below 5micromol/g efficiently so that clearly from Table 2. Moreover, it turns out that labile improves, so that the preparation temperature of a catalyst precursor is lowered.

[0034]

[Effect of the Invention] By this invention, the catalyst for AO addition reactions with good catalytic activity is acquired, and a COV value can manufacture AO adduct below 5micromol/g efficiently by using this catalyst.

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